

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-063607

(43)Date of publication of application : 29.02.2000

(51)Int.Cl.

C08L 29/04
C08K 3/32
C08K 7/00
C08L 23/08

(21)Application number : 10-236707

(71)Applicant : NIPPON SYNTHETIC CHEM IND CO
LTD:THE

(22)Date of filing : 24.08.1998

(72)Inventor : ONISHI HIDEFUMI

(54) RESIN COMPOSITION, ITS PRODUCTION, AND ITS USE**(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain a resin composition having excellent moldability and giving a film excellent in gas barrier properties by incorporating an ethylene-vinyl acetate copolymer saponificate with a phosphoric acid compound and a water- swellable layered inorganic compound.

SOLUTION: This composition comprises 100 pts.wt. ethylene-vinyl acetate copolymer saponificate, 10-1,000 ppm, based on the entire composition, of phosphoric acid or a phosphoric acid compound such as an alkali metal hydrogenphosphate, at most 30 pts.wt. water-swellable layered inorganic compound, another thermoplastic resin, and additives such as a plasticizer, a heat stabilizer, an antioxidant, a filler, or an antistatic agent. The ethylene-vinyl acetate copolymer saponificate used is one having an ethylene content of 10-60 mol.%, a degree of saponification of at least 80 mol.%, and a melt index of 0.5-50 g/10 min (at 210°C). The water-swellable layered inorganic compound is exemplified by smectite or vermiculite and has a swelling power of 30 ml/2 g at 20°C in a mixed solvent having 70/30 wt.% water/alcohol weight ratio.

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]A resin composition which contains an ethylene-vinyl acetate system copolymer saponification thing (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C), and is characterized by things.

[Claim 2]The resin composition according to claim 1, wherein ethylene contents of an ethylene-vinyl acetate system copolymer saponification thing (A) are 10 - 60-mol % and the degree of saponification is more than 80 mol %.

[Claim 3]The resin composition according to claim 1 or 2, wherein content of a phosphoric acid compound (B) is 10-1000 ppm in phosphoric acid root conversion to the whole resin composition.

[Claim 4]claims 1-3, wherein a water swelling laminar inorganic compound (C) has not less than 30ml/2 g swelling power (a measurement standard: Japanese bentonite industrial meeting standard-testing-method constant volume method) to a partially aromatic solvent of water/alcohol =70 / 30 (weight ratio) in 20 ** -- either -- a resin composition of a statement.

[Claim 5]claims 1-4, wherein a water swelling laminar inorganic compound (C) is a smectite or a water swelling fluoride mica system mineral -- either -- a resin composition of a statement.

[Claim 6]claims 1-5, wherein content of a water swelling laminar inorganic compound (C) is 30 or less weight sections to ethylene-vinyl acetate system copolymer saponification thing (A) 100 weight section -- either -- a resin composition of a statement.

[Claim 7]In manufacturing a resin composition containing an ethylene-vinyl acetate system copolymer saponification thing (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C), Water is added after making a partially aromatic solvent of water/alcohol =0 / 100 - 50/50 (weight ratio) distribute a water swelling laminar inorganic compound (C), After adjusting to water/alcohol =90 / 10 - 51/49 (weight ratio) and swelling a water swelling laminar inorganic compound (C), A manufacturing method of a resin composition mixing an ethylene-vinyl acetate system copolymer saponification thing (D) which contains a phosphoric acid compound (B) in a resin composition (1) produced by mixing an ethylene-vinyl acetate system copolymer saponification thing (A).

[Claim 8]A manufacturing method of the resin composition according to claim 7 mixing beforehand an ethylene-vinyl acetate system copolymer saponification thing (A) solution dissolved in a partially aromatic solvent of water/alcohol =90 / 10 - 51/49 (weight ratio).

[Claim 9]a claim -- a layered product which makes a resin composition of a statement at least one layer

one to 8 either.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The ethylene-vinyl acetate system copolymer saponification thing in which this invention contains a water swelling laminar inorganic compound. (EVOH is outlined hereafter) It is related with a resin composition which was excellent in gas barrier property and a moldability in more detail and a manufacturing method for the same, and its use about a resin composition and a manufacturing method for the same, and its use.

[0002]

[Description of the Prior Art]Generally, the ethylene-vinyl acetate system copolymer saponification thing (it outlines the following EVOH) is excellent in transparency, antistatic property, oil resistance, solvent resistance, gas barrier property, a smell retaining property, etc., and is thermoplastics in which melt molding is possible.

It is used for various wrapping uses, such as food packing.

However, such EVOH has the fault that gas barrier property and a mechanical physical property change with change of the environment of external humidity and temperature a lot. On the other hand, it is indicated by recent years that the mixed material of EVOH and a water swelling inorganic compound is capturing the spotlight for the purpose of the improvement of gas barrier property, for example, mixes EVOH and water swelling phyllosilicate under existence of water at JP,5-39392,A.

[0003]

[Problem(s) to be Solved by the Invention]However, as a result of this invention person's inquiring in detail, in the above-mentioned indication art. In order to supply water swelling phyllosilicate under existence of water, it is easy to generate what is called insoluble, Therefore, it becomes clear that it cannot distribute to homogeneity and time most for carrying out uniform dispersion is needed, or, In the mixed material of EVOH and water swelling phyllosilicate, there is a problem of being easy to thicken temporally, many holdups occurring at the time of extrusion, and a stripe, a fish eye, coloring, etc. occurring in a molded product at the time of long-run shaping, and it became clear that it was not still satisfactory. When the resin composition obtained by this gazette indication art was produced with extrusion, it became clear that the gas barrier property of the film after performing long-run shaping with the film at the time of starting for several hours had a problem that a difference arises. Then, it aims at providing a resin composition in which the film which is excellent in molding workability, is stabilized in this invention under such a

background, and is excellent in gas barrier property is obtained and a manufacturing method for the same, and its use.

[0004]

[Means for Solving the Problem]Then, as a result of repeating research wholeheartedly in light of the above-mentioned circumstances, this invention person found out that a resin composition containing EVOH (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C) agreed for the above-mentioned purpose, and completed this invention.

[0005]In manufacturing a resin composition containing EVOH (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C) in this invention, Water is added after making a partially aromatic solvent of water/alcohol =0 / 100 - 50/50 (weight ratio) distribute a water swelling laminar inorganic compound (C), After adjusting to water/alcohol =90 / 10 - 51/49 (weight ratio) and swelling a water swelling laminar inorganic compound (C), It faces mixing a manufacturing method of a resin composition which mixes EVOH (D) which contains a phosphoric acid compound (B) in a resin composition (1) produced by mixing EVOH (A), especially EVOH (A), A manufacturing method which mixes beforehand an EVOH (A) solution dissolved in a partially aromatic solvent of water/alcohol =90 / 10 - 51/49 (weight ratio) is preferred, and demonstrates an effect of this invention notably.

[0006]

[Embodiment of the Invention]Below, this invention is explained in detail. Especially as EVOH (A) used for this invention, although not limited, ethylene contents are 10 - 60-mol %, and it is preferred that the degree of saponification is more than 80 mol %. An ethylene content is 20-50-mol % preferably, and the degree of saponification is more than 90 mol % preferably. If the gas barrier property at the time of highly humid and melt molding nature fall less than [10 mol %] and an ethylene content exceeds 60-mol %, sufficient gas barrier property is no longer acquired, and it is not desirable. Gas barrier property, thermal stability, and moisture resistance fall, and the degree of saponification is not preferred less than [80 mol %].

[0007]As for the melt index (MI) of this EVOH (A), it is preferred that they are 0.5-50g/10 minutes (210 **), and also it is preferred that they are 1-35g/10 minutes (210 **). The inside of an extrusion machine will be in a high torque state at the time of shaping, and, in extrusion, this melt index (MI) becomes difficult, in being smaller than this range, and when larger than this range, the mechanical strength of a molded product is insufficient and it is not desirable.

[0008]This EVOH (A) is obtained by saponification of an ethylene-vinyl acetate system copolymer, and this ethylene-vinyl acetate system copolymer, It is manufactured by the publicly known arbitrary polymerizing methods, for example, suspension polymerization, emulsion polymerization, solution polymerization, etc., and saponification of an ethylene-vinyl acetate system copolymer can also be performed by a publicly known method.

[0009]If this EVOH (A) is little in the range which does not spoil the characteristics, such as transparency, gas barrier property, and solvent resistance, Alpha olefins, such as propylene, isobutene, alpha-octene, alpha-dodecen, and alpha-octadecene, Unsaturated carboxylic acid or its salt, partial alkyl ester, perfect alkyl ester, It does not interfere, even if comonomers, such as an unsaturation sulfonic acid system compound, acrylonitrile (meta), acrylamide (meta), vinyl ether, a vinyl silane compound, VCM/PVC, and styrene, are included as a copolymer component. In the range which does not spoil the meaning of this invention, even if urethane-izing, acetalization, cyanoethylation, etc. back-denaturalize, it does not

interfere.

[0010]As for a phosphoric acid compound (B), it is preferred to make 10-1000 ppm contain by phosphoric acid root conversion to the whole resin composition, and also it is preferred to make 20-150 ppm contain especially 20-500 ppm. If this content cannot acquire the effect of this invention in less than 10 ppm but exceeds 1000 ppm, fish eyes occur frequently to a molded product, an appearance defect is caused, and it is not desirable.

[0011]As a phosphoric acid compound (B), can mention phosphoric acid, the phosphate of an alkaline metal, etc. and here as an example of the phosphate of an alkaline metal, Although the hydrogen phosphate salt of an alkaline metal and the 2nd or 3rd phosphate of an alkaline metal are mentioned and phosphoric acid 1 hydrogen sodium, a sodium dihydrogenphosphate, dibasic potassium phosphate, potassium dihydrogen phosphate, etc. are illustrated as a hydrogen phosphate salt of an alkaline metal, A sodium dihydrogenphosphate and potassium dihydrogen phosphate are used more suitably. As the 2nd or 3rd phosphate of an alkaline metal, dibasic potassium phosphate, disodium hydrogen-phosphate, tribasic potassium phosphate, and phosphoric acid 3 sodium are mentioned. They are used, these being independent or using them together.

[0012]In this invention, as a method of making a resin composition containing a phosphoric acid compound (B), There is also a method which EVOH (A) and a water swelling laminar inorganic compound (C) are made to contain as EVOH (D) like the after-mentioned besides [which makes a phosphoric acid compound (B) contain in arbitrary shape as it is] a method which makes EVOH contain a phosphoric acid compound (B), and contains a phosphoric acid compound (B). About this EVOH, it is arbitrarily used out of the above-mentioned EVOH (A) and same EVOH.

[0013]As a water swelling laminar inorganic compound (C) used for this invention, Without being restricted especially Argillite, such as a smectite and a vermiculite, Synthetic mica etc. are mentioned and montmorillonite, beidellite, nontronite, saponite, hectorite, a sauconite, a SUCHIBUN site, etc. are mentioned as an example of the former smectite. These may be natural things or could be compounded. Montmorillonite is preferred also the inside of these or a smectite, especially in it. Water swelling fluoride mica system minerals, such as Na-type fluoride 4 silicon mica, a Na-type TENIO light, Li type TENIO light, and Na-type hectorite, etc. are used preferably.

[0014]The swelling power of this water swelling laminar inorganic compound (C), In 20 **, it is desirable, and it becomes insufficient [2 g / gas barrier property] in less than 30ml /that not less than 40ml/2 g not less than 30ml/2 g is not less than 50ml/2 g still more preferably preferably to the partially aromatic solvent of water/alcohol =70 / 30 (weight ratio), and it is not preferred. The swelling power of a water swelling laminar inorganic compound (C) is a Japanese bentonite industrial meeting. It is measured by a standard-testing-method constant volume method.

[0015]As for the loadings of this water swelling laminar inorganic compound (C), it is preferred that they are 30 or less weight sections to EVOH(A)100 weight section, and they are 1 - 15 weight section especially preferably 0.5 to 20 weight section more preferably. If these loadings exceed 30 weight sections, melt molding nature becomes poor and is not preferred.

[0016]Although the resin composition of this invention is obtained in this way from EVOH (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C), Especially about the manufacturing method of this resin composition, it is not limited but For example, EVOH (A), Mix the

ingredient which remains after mixing two arbitrary ingredients in a phosphoric acid compound (B) and a water swelling laminar inorganic compound (C), or, Mixing three ingredients to a package and mixing as EVOH (D) which contains a phosphoric acid compound (B) instead of mixing a phosphoric acid compound (B) etc. is chosen suitably, and it is used.

[0017]As a method of obtaining, this EVOH (D) The powder of EVOH, a pellet, The method of carrying out specified quantity content of the phosphoric acid compound (B) in the arbitrary stages at the time of desiccation, the method of impregnating with EVOH into a phosphoric acid compound (B), etc. are mentioned at the time of post-processing at the time of saponification at the time of the method of making a phosphoric acid compound (B) granular material at arbitrary gestalten, and mixing and the arbitrary stages at the time of EVOH manufacture, i.e., a polymerization. However, it is not limited to these.

[0018]It is also preferred to face to mix EVOH (D) and the water swelling laminar inorganic compound (C) containing the above-mentioned EVOH (A), a phosphoric acid compound (B), or a phosphoric acid compound (B), and to dissolve and mix in partially aromatic solvents, such as water-alcohol.

[0019]In this invention, water is added, after making the partially aromatic solvent of water/alcohol =0 / 100 - 50/50 (weight ratio) distribute a water swelling laminar inorganic compound (C), After adjusting to water/alcohol =90 / 10 - 51/49 (weight ratio) and swelling a water swelling laminar inorganic compound (C), The manufacturing method which mixes EVOH (D) containing a phosphoric acid compound (B) is preferred, without insoluble occurring, to the resin composition (1) produced by mixing EVOH (A), it can distribute uniformly, and the effect of this invention is notably demonstrated to it. It is preferred to mix especially the EVOH (A) solution in which the partially aromatic solvent of water/alcohol =90 / 10 - 51/49 (weight ratio) was dissolved beforehand preferably.

[0020]Hereafter, the desirable manufacturing method of the resin composition of this invention is explained in full detail. First, the partially aromatic solvent of water/alcohol is made to distribute a water swelling laminar inorganic compound (C). the partially aromatic solvent of water/alcohol -- water/alcohol =0 / 100 - 50/50 (weight ratio) -- the thing of 20 / 80 - 40/60 (weight ratio) is used preferably. Except a mentioned range, the mixing ratio of this water/alcohol becomes poor [dispersibility], and does not demonstrate the effect of this invention. About alcohol, isopropyl alcohol, n-propyl alcohol, methanol, ethanol, etc. are used.

[0021]Next, water is added, and water/alcohol =90 / 10 - 51/49 (weight ratio), and after adjusting to 80 / 20 - 60/40 (weight ratio) preferably and swelling a water swelling laminar inorganic compound (C), the above-mentioned EVOH (A) is mixed. The rate of the water/alcohol at this time becomes insufficient [the solubility of EVOH (A)] except the range of 90 / 10 - 51/49 (weight ratio).

[0022]In this invention, when mixing EVOH (A), there is the method of adding in a pellet type or the shape of powder, or dissolving EVOH (A) in the partially aromatic solvent of water/alcohol beforehand, and adding as an EVOH (A) solution. It is preferred especially to add as an EVOH (A) solution in respect of compatibility, It is preferred to dissolve using the partially aromatic solvent which made the presentation of the water / alcoholic partially aromatic solvent for using this EVOH (A) solution the same composition ratio in above water/alcohol =90 / 10 - 51/49 (weight ratio). When adding as an EVOH (A) solution, to adjust to 10 to 20% of the weight of concentration preferably is desired five to 30% of the weight.

[0023]After adding further and adjusting water to water/alcohol =90 / 10 - 51/49 (weight ratio), a water swelling laminar inorganic compound (C) can be swollen by usually agitating at 20-60 ** for about 0.5 to 4 hours.

[0024] It is emitted into about 5-25 ** chilled water, or the container containing this resin solution is cooled with ice water, and it deposits as a resin composition, and it dries and the resin solution obtained in this way serves as a resin composition (1). It is not limited in particular for this desiccation, but is performed by air-drying, hot air drying, infrared ray drying, vacuum drying, etc. EVOH (D) which contains a phosphoric acid compound (B) in the obtained resin composition (1) is mixed, and the resin composition of this invention is obtained. carrying out the dry blend of the EVOH (D), or using solution form, and blending, or blending by a molten state when mixing, **** -- etc. -- it is chosen suitably.

[0025] Within limits from which the purpose of this invention is not prevented by the resin composition of this invention. It is also possible to blend other thermoplastics (polyolefine, polyamide, polyester, polystyrene, EVOH, etc.), a plasticizer, a heat stabilizing agent, an ultraviolet ray absorbent, an antioxidant, colorant, a bulking agent, a drier, a spray for preventing static electricity, etc. Metal salt of a hydrocalcite system compound, a hindered phenol system, a hindered amine system thermostabilizer, and high-class aliphatic carboxylic acid can also be added as an antigelling agent.

[0026] In this way, the resin composition of this invention is used abundantly at the use of a molded product, and is fabricated by a pellet, a film, a sheet, a container, textiles, a stick, a pipe, various mold goods, etc. by melt molding etc., and melt molding can also be again presented with it using these grinding articles (when carrying out the reuse of the recovery article etc.) and pellets. As melt molding, extrusion methods (T-die extrusion, inflation extrusion, blow molding, melt spinning, variant extrusion, etc.) and injection molding process are mainly adopted. Melt molding temperature is chosen from the range of 150-250 ** in many cases.

[0027] Although the resin composition of this invention can be used for the molded product like ****, it is preferred to use at least for one side of the layer which especially consists of this resin composition as a layered product which laminates a thermoplastic resin layer, and a layered product suitable for practical use is obtained.

[0028] In manufacturing this layered product, other substrates are laminated to one side or both sides of a layer of this invention, but as a laminating method, the following methods are mentioned, for example. [of a resin composition] However, it is not limited to these.

[0029] The water-alcoholic (or solvent) content solution of a solution coating method this resin composition ** Mai Ya Bar, A thermoplastic resin film is coated by publicly known methods, such as the roller coating methods, such as photogravure and a reverse roll method, a spray coating method, and the dip-coating method, and a layered product is produced. Then, desiccation is performed by a publicly known method. If an example is given, drying temperature should just heat 40-180 ** 5 seconds - about 5 minutes at about 60-140 ** preferably. What is necessary is just to carry out until volatile matter content will usually be 2 or less % of the weight although the volatile matter content (water, alcohol, or solvent) in a coat is removed in this desiccation. In order to raise the resin composition layer of this invention, and the adhesive strength of a thermoplastic resin film, the coat of the usual anchor coat agents (a polyurethane system, a polyester system, etc.) may be beforehand carried out on a film.

[0030] ** Carry out melting extrusion of the thermoplastics to the film of the resin composition of an extrusion coating Homoto invention, and a sheet, and produce a layered product. Melting extrusion of the resin composition of this invention is conversely carried out to substrates, such as thermoplastics, and a layered product is produced.

[0031]** Extrude the resin composition of extrusion-method this invention independently, or co-extrude with other thermoplastic thing resin, and produce a layered product. As other party resin in co-extrusion, straight-chain-shape low density polyethylene, low density polyethylene, Medium density polyethylene, high density polyethylene, an ethylene-vinylacetate copolymer, An ionomer, ethylene propylene rubber, an ethylene-acrylic ester copolymer, Polypropylene, a propylene-alpha olefin (alpha olefin of carbon numbers 4-20) copolymer, Polyolefin system resin of broad sense, such as independent or an independent or thing of copolymers or these olefins of olefins, such as polybutene and a polypentene, which carried out graft denaturation of the copolymer with unsaturated carboxylic acid or its ester, Polyester, polyamide, copolymerization polyamide, polyvinyl chloride, a polyvinylidene chloride, Acrylic resin, polystyrene system resin, vinyl ester resin, a polyester elastomer, a polyurethane elastomer, chlorinated polyethylene, chlorinated polypropylene, EVOH, etc. are mentioned. Also in the above, polypropylene, polyamide, polyethylene, an ethylene-vinyl acetate system copolymer, polystyrene, polyethylene terephthalate, etc. are preferably used from a point of the ease of co-extrusion film production, and the practicality of film properties (especially intensity). In co-extrusion, thermoplastics may be blended to the resin composition of this invention, and the resin composition of this invention may be blended to thermoplastics, or the resin which raises the adhesion of both stratification planes may be blended with at least the resin composition of this invention, or one side of thermoplastics.

[0032]As other above-mentioned laminating methods, the film of the resin composition of this invention, a sheet, and the film of other substrates and a sheet can be laminated using publicly known adhesives, such as an organic titanium compound, an isocyanate compound, a polyester system compound, and a polyurethane compound, and a layered product can also be produced. ** extrusion method is advantageous also in the above at a point producible stable.

[0033]Molded products, such as a film and a sheet, are once obtained from the resin composition of this invention, When the extrusion coat of other substrates is carried out to this or the film of other substrates, a sheet, etc. are laminated using adhesives, It is usable in substrates (paper, a metallic foil, uniaxial stretching, a biaxially oriented plastic film or a sheet, textile fabrics, a nonwoven fabric, *****, a woody side, etc.) arbitrary in addition to the aforementioned thermoplastics.

[0034]When setting a (a1, a2, ...) and other substrates, for example, a thermoplastic resin layer, to b (b1, b2, ...) for the layer of the resin composition of this invention as lamination of a layered product, If it has a film, a sheet, and the shape of a bottle, only not only in the two-layer structure of a/b, b/a/b, a/b/a, a1/a2/b, a/b1/b2, b2/b1-a/b1 / b2 grade, and arbitrary combination are possible, and arbitrary combination, such as a bimetal type, a core (a)-sheath (b) type, a core (b)-sheath (a) type, or an eccentric sheath-core type, is possible for a and b in filament shape.

[0035]Although the above-mentioned resin composition or a layered product is used for the thing of various shape as it is, it is preferred to perform stretching treatment for a physical-properties improvement, and about this extension, it may be any of uniaxial stretching and biaxial stretching and is [having extended high magnification way-wise / physical properties / as much as possible] good.

[0036]What has draw magnification high as an extension method, such as deep drawing shaping and vacuum forming besides being the roll extending method, the tenter extending method, the tubular extending method, the extension blowing method, etc., is employable. In the case of biaxial stretching, any method of a simultaneous biaxial-stretching method and a serial biaxial-stretching method is employable.

80-170 °C of extension temperature is preferably chosen from the range of about 100-160 °C.

[0037] After extension is completed in this way, subsequently heat setting is performed. Heat setting performs 80-170 °C for [2 to 600 seconds] grade heat treatments at 100-160 °C preferably, it being feasible by a well-known means, and maintaining turgescence for the above-mentioned oriented film. The obtained oriented film can perform a cooling process, a rolling process, a printing job, dry laminate processing, a solution or melting coat processing, bag manufacture processing, deep drawing, box processing, tube processing, split processing, etc. if needed.

[0038] The shape of mold goods, such as a layered product obtained in this way, may be arbitrary, and a film, a sheet, a bottle, a pipe, a filament, a variant section extrusion thing, etc. are illustrated. A film, a sheet, or a container obtained is useful like the above as various kinds of wrapping, such as common foodstuffs, a pouch-packed food, drugs, heavy chemicals, and agricultural chemicals.

[0039] Since the resin composition of this invention consists of EVOH (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C), it demonstrates the effect excellent in molding workability and the gas barrier property of the film at the time of long-run shaping.

[0040]

[Example] An example is given to below and this invention is concretely explained to it. Especially, it means a weight reference that it is with the inside of an example "part" and "%", as long as there is no notice.

120 copies of isopropyl alcohol is put into the container of 15 l. of examples, Subsequently, as a water swelling laminar inorganic compound (C), natural montmorillonite [swelling power added and agitated the 67ml/2g] 2 copy to the partially aromatic solvent of water/isopropyl alcohol = 70 / 30 (weight ratio), and obtained dispersion-liquid (b).

[0041] After having added 280 copies of water there gradually, agitating at 40 °C for 2 hours and swelling (C), 100 copies of pellets of EVOH (A1) (degree % of 99.6 mol of ethylene content % and saponification of 30 mol, melt-index (MI) 8g/10 minutes (210 °C, 2160g of load)) are added, at 90 °C, it agitated for 2 hours and complete dissolution was carried out. Next, the obtained solution was slushed into the chilled water (5 °C) of 700 copies, the resin composition was deposited, and vacuum drying was performed.

[0042] EVOH (D1) (ethylene content % of 35 mol.) which contains phosphoric acid (B) to 100 copies of resin compositions produced by drying Degree% of 99.8 mol of saponification, to EVOH, 100 copies of content of phosphoric acid mixed 100 ppm by phosphoric acid root conversion, and obtained the resin composition of this invention for melt-index (MI) 3g/10 minutes (210 °C, 2160g of load). (The content of phosphoric acid was phosphoric acid root conversion, and was 50 ppm to the whole resin composition.)

[0043] Assay of the phosphate of phosphoric acid and an alkaline metal was performed with molybdenum blue (ascorbic acid) absorption photometry according to JIS K 0102. However, the following procedure performed preparation of the sample.

1. Weigh 1 g of samples precisely and supply to a 300-ml Kjeldahl flask.
2. About 5 ml of pure water is added, and about 15 ml of concentrated sulfuric acid is dropped gradually.
3. Heat a Kjeldahl flask with a heater and remove water and sulfuric acid just before hardening by drying.
4. Add about 5 ml of concentrated sulfuric acid after cooling, cover the mouth of a Kjeldahl flask by a funnel and heat it again.

[0044] 5. After it adds several drops of concentrated sulfuric acid gradually after white smoke begins to be full in a Kjeldahl flask, and the inside of a Kjeldahl flask assumes blackish brown with NO_x gas, stop

dropping of sulfuric acid, and continue heating until it is replaced by white smoke. The sulfuric acid dropping operation under heating is repeated several times.

6. After the solution in a Kjeldahl flask presents colorlessness - yellowish green transparence, stop dropping of sulfuric acid, and drive out a part for ***** in a solution, and residual water.

7. Take out the funnel which covered the mouth of the Kjeldahl flask, ignite until it becomes a residue of 2-3 ml, and drive out sulfuric acid.

O Also carry out simultaneously the blank test which does not add a (sample) to according to.

[0045]The obtained resin composition was supplied to the single screw extruder, the film was produced under conditions with an extrusion machine preset temperature of 210 °C in T-pressure die casting, and the 30-micrometer-thick film was obtained. This film was evaluated as following.

[0046](Processability) In the film fabricating operation, the appearance on a film when continuous molding of 3 hours is performed was observed, and the following item was evaluated.

** O which evaluated the existence of SUJISUJI by the following standard ... Generating of the stripe was not seen even if processing 3 hours passed.

x ... Generating of the stripe was looked at by less than [processing 3 hour].

[0047]** The following standard estimated the existence (film size: 10 cm x 10 cm) of the fish eye fish eye.

O ... Less than [three piece] ** ... 4 - 20 piece x ... 21 or more pieces [0048]** The following standard estimated the existence of coloring coloring.

O ... Coloring was not accepted.

** ... Yellow coloring was accepted slightly.

x ... Yellow coloring was severe and use was difficult practically.

[0049](Oxygen transmittance) In the film obtained immediately after a film shaping start, and the film obtained 5 hours after a start, using OXTRAN of MOCON, at 20 °C. It measured under the conditions of 100%RH and the ratio (S2/S1) of the oxygen transmittance (S2) of the film obtained 5 hours after a start to the oxygen transmittance (S1) of the film obtained immediately after a start estimated.

O ... S2/S1 is less than [1.5] x... S2/S1 is 1.5 or more. [0050]150 copies of isopropyl alcohol and 150 copies of water are put into the container of 25 l. of examples, Subsequently, as a water swelling laminar inorganic compound (C), natural montmorillonite [swelling power added and agitated the 67ml/2g]5 copy to the partially aromatic solvent of water/isopropyl alcohol =70 / 30 (weight ratio), and obtained dispersion-liquid (**). After having added 100 copies of water there gradually, agitating at 40 °C for 2 hours and swelling (C), EVOH (A2) (degree % of 99.6 mol of ethylene content % and saponification of 30 mol.) Melt index (MI) 3g/500 copies of water-alcoholic mixed solutions (water/alcohol =50/[20% of concentration and] 50 (weight ratio)) for 10 minutes (210 °C, 2160g of load) are added, at 90 °C, it agitated for 2 hours and complete dissolution was carried out. Next, the obtained solution was slushed into the chilled water (5 °C) of 700 copies, the resin composition was deposited, and vacuum drying was performed.

[0051]EVOH (D2) (ethylene content % of 35 mol.) which contains a sodium dihydrogenphosphate (B) to 100 copies of resin compositions produced by drying Degree% of 99.8 mol of saponification, to EVOH, 300 copies of content of the sodium dihydrogenphosphate mixed 440 ppm by phosphoric acid root conversion, and obtained the resin composition of this invention for melt-index (MI)3g/10 minutes (210 °C, 2160g of load). (The content of the sodium dihydrogenphosphate was phosphoric acid root conversion, and was 110 ppm to the whole resin composition) The evaluation same about the obtained resin composition as

Example 1 was performed.

[0052]In example 3 Example 1, except having changed phosphoric acid into disodium hydrogen-phosphate, it carried out similarly and evaluated like Example 1. (The content of disodium hydrogen-phosphate was phosphoric acid root conversion, and was 60 ppm to the whole resin composition)

[0053]in example 4 Example 1 -- as a water swelling laminar inorganic compound (C) -- Na-type fluoride 4 silicon mica [-- except having used the 96ml/2g]2 copy to the partially aromatic solvent of water/isopropyl alcohol =70 / 30 (weight ratio), swelling power was performed similarly and evaluated like Example 1.

[0054]In comparative example 1 Example 1, except not having mixed EVOH (D1) containing phosphoric acid (B), but having mixed EVOH (A1) and a water swelling laminar inorganic compound (C) in the water/isopropyl alcohol =280 copy/120 copy partially aromatic solvent, it carried out similarly and evaluated like Example 1.

[0055]In comparative example 2 Example 1, natural montmorillonite was not added, but except having produced the film using the resin composition (the content of phosphoric acid is phosphoric acid root conversion, and is 75 ppm to the whole resin composition) which consists of EVOH (A1) and phosphoric acid (B), it carried out similarly and evaluated like Example 1. The result of an example and a comparative example is shown in Table 1.

[0056]

[Table 1]

Immediately after a film appearance oxygen transmittance (cc/m^2 and day-atm) ***** start (S2) 5 hours after a start Ratio Evaluation stripe fish eye coloring (S1) Example (S2/S1) 1 O O O 9 9 1.0 O ** . 2 O O O 9 9 1.0 O ** 3 O O ** 9 9 1.0 O ** 4 O ** ** 9 9 1.0 O comparative example 1 O x x 9 9 1.0 O ** 2 x x ** 17 31 1.8 x [0057]

[Effect of the Invention]Since the resin composition of this invention consists of EVOH (A), a phosphoric acid compound (B), and a water swelling laminar inorganic compound (C), it shows the effect which was excellent in the molding workability of a film, a sheet, etc., and also was excellent in the gas barrier property of the film at the time of long-run shaping. A film, a sheet, or a container is presented with these resin compositions, and they are useful as various kinds of wrapping, such as common foodstuffs, a pouch-packed food, drugs, heavy chemicals, and agricultural chemicals.

[Translation done.]